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# Isotopic Quantum Effects of Liquid Methanol

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Density functional calculations (B3LYP/6-31+G*) on molecular clusters and a Quantum Cluster Equilibrium (QCE) model have been used to calculate structural and thermodynamic properties of four isotopically labelled methanols. The method allowed to reproduce the characteristic differences in boiling points and heats of vaporisation. Also structural changes could be detected and related to recent experimental findings. It could be shown that isotopic effects clearly have a quantum-mechanical origin.

## 1 Introduction

Isotopic substitution plays an important role in chemistry and biology. For example, the protein folding reaction strongly depends on deuteration of the protein backbone or deuteration of the solvent water. In particular the change from $H_2O$ to $D_2O$ increases the strength of the solvent-solvent hydrogen bonds and significantly influences the protein folding process[1]. Thus one is interested to understand the origin of changing thermodynamic and structural properties caused by isotopic substitution. Contrary to the prediction of classical mechanics, thermodynamic and structural properties of many liquids are known to be isotopically dependent[2–6]. Although the magnitude of differences in the densities, freezing points and boiling points of many hydrogenated and deuterated liquids are well known, the nature of these differences is still not fully understood. This is in particular true for hydrogen bonded (H-bonded) liquids such as water and alcohols (Fig. 1)[7,8].

In Fig. 2 measured boiling points and heats of vaporisation are given for partial and fully deuterated liquid methanol. Plotting these thermodynamic properties in the order of increasing molecular weight, they show a typical ‘zigzag’ behaviour. Obviously increasing molecular weight does not necessarily lead to higher boiling points and heats of vaporisation. It rather seems to be important which part of the molecule is deuterated and whether

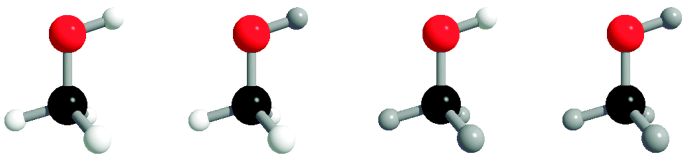


Figure 1. Isotopically labelled methanols.

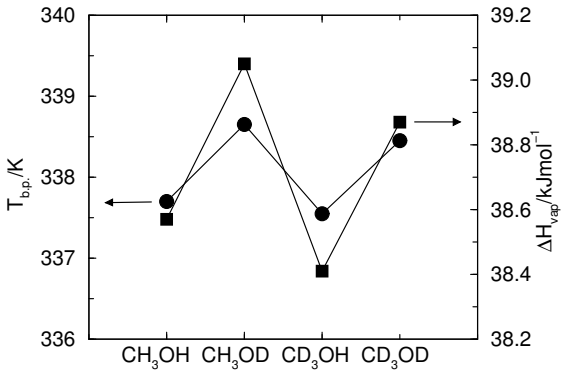


Figure 2. Measured boiling points (left) and heats of vaporisation (right) of isotopically substituted methanols.

this part is involved in hydrogen bonding or not.

In this study we used density functional calculations (B3LYP/6-31+G*) on molecular clusters and a Quantum Cluster Equilibrium (QCE) model[9–12] to study such isotope effects in liquid methanol.

## 2 Methods

The QCE theory has recently been show to provide a qualitative or semi-quantitative description of the thermodynamics of hydrogen of bonded liquids. Briefly, QCE theory is based on treatment of the simultaneously equilibria between H-bonded clusters,

$$M \rightleftharpoons \frac{1}{2} M_2 \rightleftharpoons \frac{1}{3} M_3 \rightleftharpoons \ldots \rightleftharpoons \frac{1}{n} M_n,$$

in analogy to covalent chemical equilibria. Standard methods of quantum statistical thermodynamics are employed to evaluate the equilibrium cluster populations and associated thermodynamic properties that govern phase behaviour. The necessary cluster properties (optimised structures, vibrational frequencies, binding energies) can be obtained with the help of standard ab initio programs for direct input into a QCE cluster mixture. A key feature of QCE theory is that interactions within clusters are treated in full ab initio fashion, where as residual cluster-cluster interactions are treated by a mean-field approximation. This allows the important cooperative effects of H-bond network patterns to be properly incorporated, up to the maximum cluster size permitted by computational resources. At specific temperature T and pressure P, the QCE equilibrium polynomial normally exhibits multiple roots (phases $\alpha$) of distinct molar volume V($\alpha$), where the root of lowest Gibbs free energy G($\alpha$) is the stable equilibrium phase. Calculated properties of each cluster can finally be weighted with the QCE cluster population of the chosen phase to predict thermodynamic or spectroscopic properties.

The QCE/B3LYP/6-31+G* methanol model comprises 24 molecular clusters including linear, ring and lasso like clusters. It could be shown that the liquid phase is dominated by cyclic pentamers and hexamers, whereas the gas phase is ruled mainly by monomers.

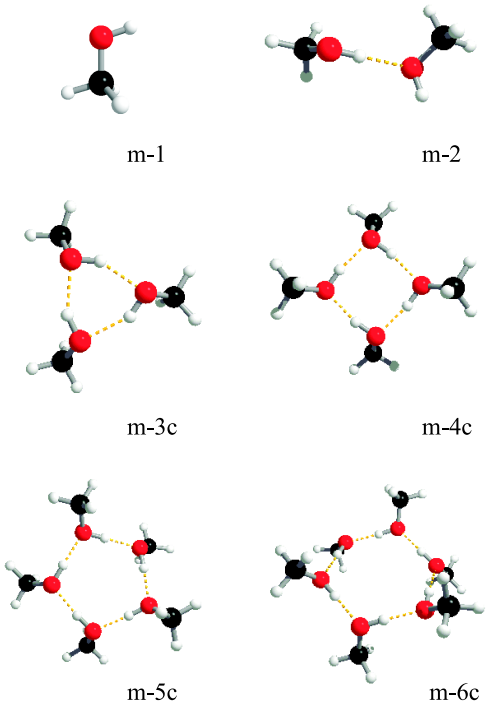


Figure 3. Selected optimised structures and labels of methanol clusters of the QCE(24)/B3LYP/6-31+G* model. The liquid phase is dominated by cyclic pentamers and hexamers, whereas the gas phase is ruled mainly by monomers.

Some selected clusters of the QCE(24)/B3LYP/6-31+G* mixture for protonated methanol are shown in Fig. 3 including the leading structures which determine the liquid and the gases phase. The total energies, raw and counterpoise corrected[13] (CPC) H-bond energies of those clusters are summarised in comparison to the methanol monomer in Tab. 1.

| Species | Total energy | $E_{\mathrm{B3LYP}}$ | $E^{\mathrm{CPC}}_{\mathrm{B3LYP}}$ |
|---|---|---|---|
| $M_1$ | -115.725193 | | |
| $M_2$ | -231.460342 | -26.14 | -21.62 |
| $M_{3c}$ | -347.203411 | -73.07 | -64.01 |
| $M_{4c}$ | -462.952816 | -136.64 | -117.92 |
| $M_{5c}$ | -578.694033 | -178.71 | -153.72 |
| $M_{6c}$ | -694.435172 | -220.57 | -190.66 |

Table 1. Total energies, raw and counterpoise-corrected binding energies $E_{\mathrm{B3LYP}}$ and $E^{\mathrm{CPC}}_{\mathrm{B3LYP}}$, for all $CH_3OH$, $CH_3OD$, $CD_3OH$, and $CD_3OD$ methanol clusters, calculated at the B3LYP/6-31+G* level. Total energies in hartree, all other values in kJ/mol.

The removal of BSSE is indispensable because the important cooperative effects are systematically underestimated at uncorrelated levels in particular using small basis sets. All optimised clusters of Fig. 3 were found to have only positive frequencies, demonstrating that they are all true equilibrium species on the B3LYP/6-31+G* potential energy surface[14]. For the present work, all input cluster properties are recalculated for the deuterated methanol clusters. Therefore, the initial frequency calculation for each protonated cluster is followed by a second thermochemistry analysis using the same temperature and pressure, but a different selection of isotopes. The analysis uses the standard expressions for an ideal gas in the canonical ensemble. Details can be found in McQuarrie[15] and other standard statistical mechanics texts. The Born-Oppenheimer approximation is based on the approximation that the nuclei are so much more massive than the electrons that it is legitimate to calculate the electronic state of a molecule in a field of a fixed nuclei. Thus the isotopic substituted methanol clusters all have the same internuclear potential function, and therefore have the same force constants, the same depth of the potential $D_e$ and the same internuclear separation.

In the framework of QCE the total canonical partition function can be expressed as

$$Q = \prod_{i=1}^{c} Q_i(n_i, V, T) = \prod_{i=1}^{c} \frac{q_i^{n_i}}{n_i!}, \tag{1}$$

where $n_i$ denotes the number of clusters of type i and $q_i$ the partition function for clusters of type i. We assume that each cluster partition function $q_i$ can be factored in the usual way into translational, rotational, vibrational, and electronic contributions. The total canonical partition function Q for the isotopic species vary, where the different masses of the molecular clusters change the cluster partition function $q_i$.

In the translational partition function $q_{i,trans}$

$$q_{i,trans} = \frac{V - V_{excl}}{\Lambda^3}, \tag{2}$$

where

$$\Lambda = \frac{h}{(2\pi mkT)^{1/2}} \tag{3}$$

is the thermal de Broglie wavelength, the mass m of the cluster species is increased by replacing protons through deuterons. In the rotational partition function $q_{i,rot}$

$$q_{i,rot} = \frac{\sqrt{\pi}}{\sigma} \left( \frac{T^3}{\Theta_A \, \Theta_B \, \Theta_C} \right)^{\frac{1}{2}}, \tag{4}$$

the rotational temperatures

$$\Theta_A = \frac{\hbar^2}{2I_A k}, etc \tag{5}$$

determined from calculated moments of inertia $I_A$, $I_B$ and $I_C$ are reduced by deuteration.

In the vibrational partition function $q_{i,vib}$

$$q_{i,vib} = \prod_{j=1}^{3N-6} \left(1 - e^{-\theta_j/T}\right)^{-1}, \tag{6}$$

where

$$\theta_j = \frac{h\,\nu_j}{k}, etc. \tag{7}$$

are the vibrational temperatures $\theta_j$, the vibrational frequencies $\nu_j$ become lower upon deuteration. And finally, in the electronic partition function $q_{i,elec}$

$$q_{i,elec} = e^{(E_{HF}^{(CP)} - E_{Ref})/kT}, \tag{8}$$

where

$$E_{B3LYP}^{(CP)}(M_i) = E_{B3LYP}(M_i) + \Delta E_{CP}(M_i) + \Delta E_{ZPE}(M_i) + \Delta E_{mf}(M_i) \tag{9}$$

is the counterpoise corrected energy for each cluster, the vibrational zero point energy correction $\Delta E_{ZPE}$ is reduced by moving from light to heavy methanol.

Two parameters, correcting the estimate of excluded cluster volume $V_{exl}$ in the translational partition function and taking into account cluster-cluster-interactions by a mean-field correction $\Delta E_{mf}(M_i)$ in the electronic partition function are kept constant with respect to QCE studies of protonated methanol[16].

| Species | $\Theta_X^{CH_3OH}$ | $\Theta_X^{CH_3OD}$ | $\Theta_X^{CD_3OH}$ | $\Theta_X^{CD_3OD}$ |
|---|---|---|---|---|
| $M_1$ | 6.101 | 5.263 | 3.379 | 3.104 |
| | 1.181 | 1.120 | 0.950 | 0.902 |
| | 1.140 | 1.053 | 0.924 | 0.859 |
| $M_{5c}$ | 0.033 | 0.033 | 0.028 | 0.028 |
| | 0.032 | 0.031 | 0.027 | 0.027 |
| | 0.020 | 0.019 | 0.017 | 0.017 |
| $M_{6c}$ | 0.022 | 0.021 | 0.019 | 0.018 |
| | 0.022 | 0.021 | 0.018 | 0.018 |
| | 0.016 | 0.013 | 0.012 | 0.011 |

Table 2. Rotational temperatures $\Theta_A$, $\Theta_B$,and $\Theta_C$ for $CH_3OH$, $CH_3OD$, $CD_3OH$ and $CD_3OD$ methanol clusters. All values in K.

The merit of QCE is now that we can calculate the microstructural composition and thermodynamical properties for all four isotopic substituted methanol clusters. It is interesting to see whether the calculated properties change through replacing the protonated by deuterated methanol clusters in the expected and experimentally found way. The results can than be analysed by examining separately the isotopic shifts produced by changes in

| Species | $\nu_1$ | $\nu_2$ | $\nu_3$ | $\nu_4$ | $\nu_5$ |
|---|---|---|---|---|---|
| $M_1^{CH_3OH}$ | 421.815 | 1349.222 | 1380.532 | 1508.879 | 1754.973 |
| $M_1^{CH_3OD}$ | 334.649 | 1107.881 | 1355.319 | 1508.808 | 1607.438 |
| $M_1^{CD_3OH}$ | 400.856 | 1105.807 | 1162.082 | 1281.778 | 1406.752 |
| $M_1^{CD_3OD}$ | 307.308 | 993.284 | 1162.011 | 1273.839 | 1364.254 |
| $M_{5c}^{CH_3OH}$ | 9.594 | 28.498 | 50.196 | 60.475 | 67.373 |
| $M_{5c}^{CH_3OD}$ | 9.915 | 28.631 | 50.098 | 59.950 | 66.839 |
| $M_{5c}^{CD_3OH}$ | 8.980 | 25.810 | 44.473 | 53.498 | 59.888 |
| $M_{5c}^{CD_3OD}$ | 8.962 | 25.783 | 44.180 | 53.044 | 59.345 |
| $M_{6c}^{CH_3OH}$ | 21.404 | 22.570 | 33.651 | 46.324 | 47.900 |
| $M_{6c}^{CH_3OD}$ | 21.360 | 22.526 | 33.633 | 46.093 | 47.455 |
| $M_{6c}^{CD_3OH}$ | 19.331 | 20.434 | 30.171 | 40.664 | 43.290 |
| $M_{6c}^{CD_3OD}$ | 19.295 | 20.399 | 30.153 | 40.459 | 42.987 |

Table 3. Low-lying vibrational frequencies for $CH_3OH$, $CH_3OD$, $CD_3OH$ and $CD_3OD$ methanol clusters dominating the gaseous and the liquid phases. All values in K.

the translational masses, the rotational temperatures, the vibrational frequencies and the vibrational zero point energies, as given in Tab. 2, 3 and 4 for the methanol clusters $CH_3OH$, $CH_3OD$, $CD_3OH$ and $CD_3OD$.

A this point we should mention that we calculated more protonated methanol clusters than presented up to now. Already in the earlier QCE(24)/B3LYP/6-31+G* mainly clusters with characteristic structures, binding energies and normal modes were considered. Isomers showing energy differences that are smaller than those separating distinct cluster topologies were not taken into account. In our view it is sufficient to include only a 'representative 'conformer of each topology class to evaluate the cluster equilibria that are the most relevant to structural and spectroscopic properties. As said for deuteration we have chosen only clusters which survived the QCE(24)//B3LYP/6-31+G* procedure for enthalpic and entropic reasons.

| | $CH_3OH$ | | $CH_3OD$ | | $CD_3OH$ | | $CD_3OD$ | |
|---|---|---|---|---|---|---|---|---|
| | $\Delta E_{\mathrm{ZPE}}$ | $E_{\mathrm{diss}}$ | $\Delta E_{\mathrm{ZPE}}$ | $E_{\mathrm{diss}}$ | $\Delta E_{\mathrm{ZPE}}$ | $E_{\mathrm{diss}}$ | $\Delta E_{\mathrm{ZPE}}$ | $E_{\mathrm{diss}}$ |
| $M_2$ | 6.18 | -15.44 | 5.15 | -16.47 | 5.89 | -15.73 | 5.33 | -16.29 |
| $M_{3c}$ | 14.83 | -49.18 | 12.54 | -51.47 | 14.31 | -49.70 | 12.03 | -51.98 |
| $M_{4c}$ | 24.22 | -93.70 | 20.62 | -97.30 | 23.35 | -94.57 | 19.79 | -98.13 |
| $M_{5c}$ | 29.52 | -124.20 | 25.18 | -128.54 | 28.44 | -125.28 | 24.20 | -129.52 |
| $M_{6c}$ | 35.32 | -155.34 | 30.06 | -160.60 | 33.89 | -156.77 | 28.89 | -161.77 |

Table 4. Absolute zero-point vibrational differences $\Delta E_{\mathrm{ZPE}}$, and absolute dissociation energies $E_{\mathrm{diss}}$, of $CH_3OH$, $CH_3OD$, $CD_3OH$, and $CD_3OD$ methanol clusters, calculated at the B3LYP/6-31+G* level. All values in kJ/mol.

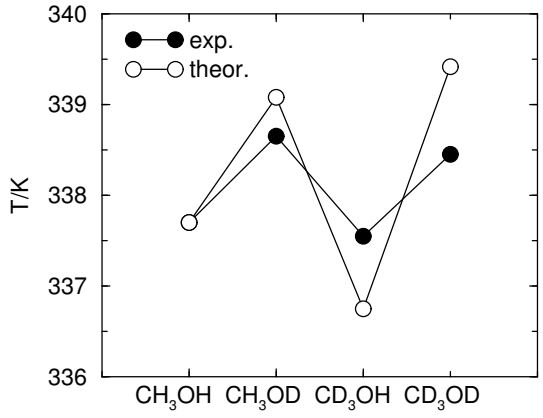


Figure 4. Measured and calculated boiling points of isotopically labelled methanols.

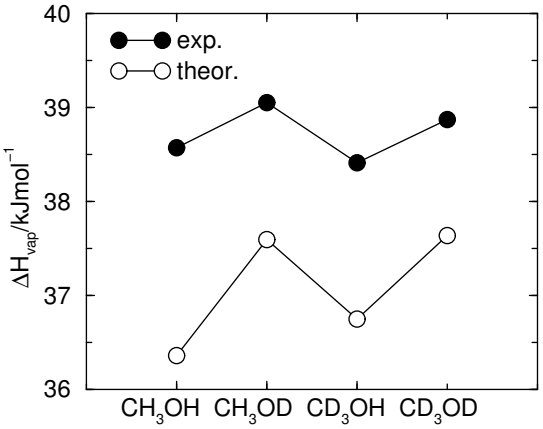


Figure 5. Measured and calculated heats of vaporisation of isotopically labelled methanols.

## 3 Results and Discussion

### 3.1 Thermodynamical Properties

The method allows to reproduce the characteristic differences in boiling points (Fig. 4) and heats of vaporisation (Fig. 5) of the isotopically substituted methanols. Regarding the properties for the leading cluster species in the gas and in the liquid phase (Tab. 3 and 4) this behaviour can be understood. In general the boiling points and heats of vaporisation increase by deuteration, in particular if the deuterated part of the molecule is involved in hydrogen bonding. Studying the influence of the isotopic effect individually on each partition function, we could conclude that the characteristic 'zigzag' behaviour of the thermodynamic properties is determined by zero-point energies (enthalpic effect) and the vibrational

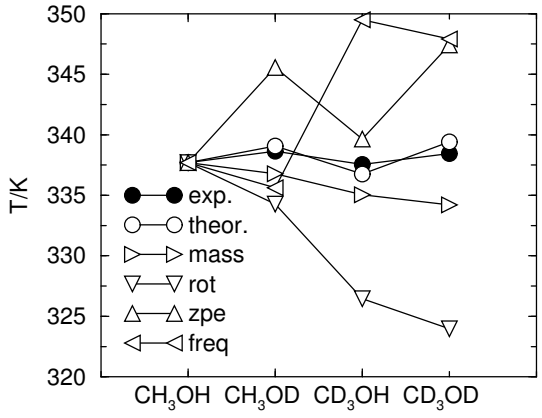


Figure 6. Calculated B3LYP/6-31+G* boiling points for isotopically labelled methanols. It is shown by altering the partition functions individually that the 'zigzag'behaviour is mainly caused by zero point energies.

frequencies (entropic effect) of the isotopically substituted methanol clusters (Fig. 6). The strongly pronounced 'zigzag' behaviour caused by changing zero point energies is slightly balanced by vibrational frequencies of the deuterated clusters showing the opposite effect. It could be shown that isotopic effects clearly have a quantum-mechanical origin.

### 3.2 Structural Properties

Even if we cannot reproduce the full structure of liquid methanol, the characteristic features and differences of the isotopically labelled methanols can be obtained. In Fig. 7 it can be seen that the contribution of the methanol hexamer, the strongest H-bonded cluster

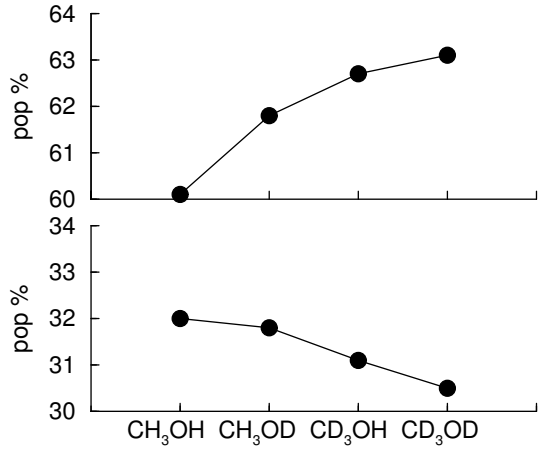


Figure 7. Hexamer (above) and pentamer (below) populations at 298 K for all isotopic substituted methanols.

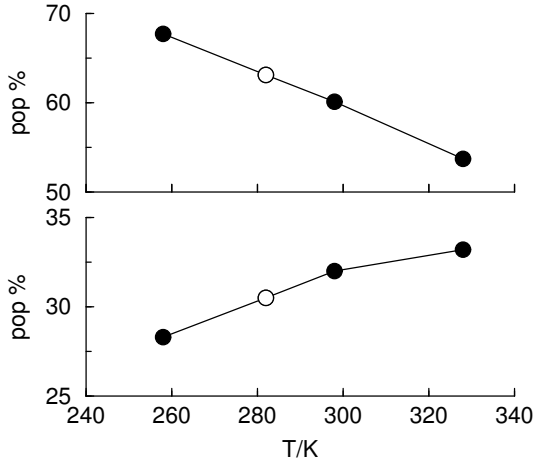


Figure 8. Hexamer (above) and pentamer (below) populations for fully deuterated methanol as a function of temperature. Deuterated methanol is stronger structured than protonated. The calculated structural temperature shift is 16 K (from 298 K to 282 K).

species, increases as a function of isotopic substitution for account of methanol pentamers. Regarding the temperature dependent shifts of the cluster populations in Fig. 8 we see that the cluster composition for $CD_3OD$ at 298 K is found at 282 K for $CH_3OH$. Protonated methanol is stronger disordered than deuterated methanol at the same temperature. In other words: There is a structural temperature shift of about 16 K which is in agreement with experimental findings[17–20]. This knowledge will be useful in correcting neutron diffraction hydrogen-deuterium substitution experiments, where the differences in the intermolecular structure between isotopic samples is usually assumed to be zero.

## 4 Summary

We have demonstrated that the simple QCE//B3LYP/6-31+G* treatment of isotopically substituted methanol is able to reproduce the typical 'zigzag' behaviour of the boiling point and the heat of vaporisation. This behaviour is mainly determined by zero point energies. The boiling point is only slightly increased by deuteration of the methyl group but strongly increased by deuteration of the hydroxyl group which is involved in hydrogen bonding. The characteristic 'zigzag' behaviour is softened by the low vibrational frequencies of the isotopically labelled species. Overall, we can conclude that the isotopic effects have clearly a quantum-mechanical origin and that they are in particular strong for H-bonded liquids.

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